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Certificate

REPUBLIC OF SOUTH AFRICA

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the documents annexed hereto are true copies of:

Application forms P.1, P2 and provisional specification of South African Patent Application No. 2003/7773 as originally filed in the Republic of South Africa on 6 October 2003 in the name of SASOL TECHNOLOGY (PTY) LTD for invention entitled: "TANDEM OLIGOMERIZATION-COPOLYMERIZATION OF OLEFINS."

Getekken te  
Signed at  
PRETORIA

in die Republiek van Suid-Afrika, hierdie  
in the Republic of South Africa, this

19<sup>th</sup> dag van  
day of May 2004

1 Registrar of Patents

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## REGISTER OF PATENTS

OFFICIAL APPLICATION NO.	LODGING DATE: PROVISIONAL	ACCEPTANCE DATE	
21 01 2003 / 7773	22 6 Oct 2003	47	
INTERNATIONAL CLASSIFICATION	LODGING DATE: COMPLETE	GRANTED DATE	
51	23		
INTERNATIONAL APPLICATION NO.	LODGING DATE: INTERNATIONAL		
FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)			
71	SASOL TECHNOLOGY (PTY) LTD		
APPLICANTS SUBSTITUTED:		DATE REGISTERED	
71			
ASSIGNEE(S)		DATE REGISTERED	
71			
FULL NAME(S) OF INVENTOR(S)			
72	DE WET-ROOS, Deon; DIXON, John, Thomas		
PRIORITY CLAIMED NB - Use International abbreviation for country (See Schedule 4)	COUNTRY	NUMBER	DATE
	33	31	32
TITLE OF INVENTION		5	
TANDEM OLIGOMERIZATION-COPOLYMERIZATION OF OLEFINS			
ADDRESS OF APPLICANT(S)/PATENTEE(S)			
1 STURDEE AVENUE, ROSEBANK, 2196 JOHANNESBURG, SOUTH AFRICA			
ADDRESS FOR SERVICE		REF	
74	HAHN & HAHN INC, PRETORIA		F489
PATENT OF ADDITION NO.		DATE OF ANY CHANGE	
61			
FRESH APPLICATION BASED ON		DATE OF ANY CHANGE	

## FORM P1

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT  
[Section 30 (1) - Regulation 22]

Revenue stamps or revenue franking machine impression

Official date stamp

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.

21 01 2003 / 7773

(i) APPLICANT'S OR AGENT'S REFERENCE  
F489

(ii) FULL NAME(S) OF APPLICANT(S)

71 SASOL TECHNOLOGY (PTY) LTD

(iii) ADDRESS(ES) OF APPLICANT(S)

1 STURDEE AVENUE, ROSEBANK, 2196 JOHANNESBURG, SOUTH AFRICA

(iv) TITLE OF INVENTION

54 TANDEM OLIGOMERIZATION-COPOLYMERIZATION OF OLEFINS

(v) The applicant claims priority as set out on the accompanying form P2.  
The earliest priority claimed is Country: Number: Date:

(vi) This application is for a patent of addition to Patent Application No.

21 01

(vii) This application is a fresh application in terms of section 37 and is based on Patent Application No.

21 01

(viii) This application is accompanied by:

1. A single copy of a provisional or two copies of a complete specification of 20 pages.
2. Drawings of \_\_\_ sheets
3. Publication particulars and abstract (form P8 in duplicate).
4. A copy of Figure \_\_\_ of the drawings for the abstract.
5. An assignment of invention.
6. Certified priority document(s) (state number).
7. Translation of the priority document(s).
8. An assignment of priority rights.
9. A copy of the form P2 and the specification of SA Patent Application No.
10. A declaration and power of attorney form P3.
11. Request for ante-dating on form P4.
12. Request for classification on form P9.
13. In terms of section 31(1) the applicant has added additional revenue stamps to this form for claiming priority after 12 months but before 15 months from the priority filing date.
14. Form P2 + copy

21 01

(ix) 74 Address for service: HAHN &amp; HAHN INC, 222 Richard Street, HATFIELD, 0083, Pretoria

Dated this 6 day of October 2003

PLM

Signature of applicant(s) or agent

This duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with an official stamp

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Official date stamp
2003 -10- 06
Registrar of Patents
REGISTRATEUR VAN PATENTE, MODDELLE, HANDELSMERKE EN OUTEURSREG

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
**PROVISIONAL SPECIFICATION**  
[Section 30(1) - Regulation 27]

OFFICIAL APPLICATION NO	
21	01
2003/7773	

LODGING DATE	
22	6 Oct 2003

FULL NAME(S) OF APPLICANT(S)	
71	SASOL TECHNOLOGY (PTY) LTD

FULL NAME(S) OF INVENTOR(S)	
72	DE WET-ROOS, Deon; DIXON, John, Thomas

TITLE OF INVENTION	
i4	TANDEM OLIGOMERIZATION-COPOLYMERIZATION OF OLEFINS

2003/7773

**Title: Tandem oligomerization-copolymerization of olefins**

**Technical field of the invention**

This invention relates to a tandem oligomerization and copolymerization catalyst system and process for the production of branched polyolefins wherein the polymerization catalyst can be homogeneous or in-situ supported on a support medium.

**Background to the invention**

This invention relates to a catalyst system, which facilitates the production of 1-octene or 1-hexene in high selectivity on the one hand, in combination with a suitable polymerization catalyst on the other hand so that in-situ copolymerization of the formed  $\alpha$ -olefins with the available ethylene feedstock take place. Preferably, oligomerisation and copolymerisation take place at the same time under the same reaction conditions.

With regard to the oligomerization catalyst, it is known from prior art (US patent 6,184,428) that a nickel catalyst comprising a chelating ligand, preferably 2-diphenyl phosphino benzoic acid (DPPBA), a nickel precursor, preferably  $\text{NiCl}_6 \cdot 6\text{H}_2\text{O}$ , and a catalyst activator, preferably sodium tetraphenylborate, catalyse the oligomerization of ethylene to yield a mixture of linear olefins containing considerable quantities of 1-octene. The selectivity towards linear C8  $\alpha$ -olefins is claimed to be 19%. Similarly the Shell Higher Olefins Process (SHOP process, (US patents 3,676,523 and 3,635,937) using a similar catalyst system is reported to typically yield 11 mass % 1-octene in its product mixture (Chem Systems PERP reports 90-1, 93-6 and 94/95S12).

Similarly, Ziegler-type technologies based on trialkylaluminium catalysts, independently developed by Gulf (Chevron, e.g. DE patent 1,443,927) and Ethyl

Corporation (BP/Amoco, e.g. US patent 3,906,053), are also commercially used to oligomerize ethylene to mixtures of olefins that reportedly contain 13-25 mass % 1-octene (Chem Systems PERP reports 90-1, 93-6, and 94/95S12).

Moreover, chromium-based catalysts containing heteroatomic ligands with both phosphorous and nitrogen heteroatoms selectively catalyse the trimerization of ethylene to 1-hexene. An example of such a heteroatomic ligand for ethylene trimerization includes  $(\text{o-methoxy-phenyl})_2\text{PN}(\text{Me})\text{P}(\text{o-methoxy-phenyl})_2$  (WO 02/04119). Since these catalyst systems are very specific for the production of 1-hexene, they only yield 1-octene as an impurity (typically less than 3 mass % of the product mixture as disclosed by WO 02/04119).

Although examples of heterogeneous polymerization catalysts abound that mention the copolymerization of in-situ formed  $\alpha$ -olefins as by-products of the polymerization process, few examples are available describing the deliberate combination of a heterogeneous polymerization catalyst on a support and a homogeneous oligomerization catalyst, or the deliberate combination of two homogeneous catalysts systems where one system produces an  $\alpha$ -olefin and the other catalyst copolymerizes the olefin formed in-situ as a comonomer with ethylene.

It is well-known in the open literature that variation of reaction conditions such as pressure, temperature, feed gas make-up, comonomer content etc. result in polymers with desirable physical properties such as tear-strength, optical clarity, elasticity and many other physical properties deemed desirable by polymer end-users. In particular, the production of linear low-density polyethylene sees the co-polymerization of high purity  $\alpha$ -olefins such as 1-butene, 1-hexene and 1-octene to produce LLDPE suitable for films and sheets, blow molding, extrusion and wire and cable jacket material as well as rotational molding material.

The high selectivity towards 1-octene or 1-hexene of the present oligomerization catalyst in combination with a suitable polymerization catalyst can therefore result in a process that produces polyethylene grades with high end-user specifications without the need of a separate facility or process to manufacture the polymer.

Some of the advantages of having such a tandem oligomerization/copolymerization process are the following:

- Reduced capital outlay for the construction of separate plants for the production of  $\alpha$ -olefins and polyethylene such as LLDPE
- Reduced variable operating costs such as:
  - Buying of high-purity  $\alpha$ -olefins
  - Transport of harmful chemicals
  - Storage and possible contamination of olefins
  - Safety and operational hazards associated with storage and handling of olefins
- The ability to produce a superior LLDPE of various grades by simply manipulating the ability to convert  $\alpha$ -olefin formation from hexene to octene by judicious choice of the ligand system of the oligomerization catalyst
- The additional opportunity of producing not only LLDPE but also additional products such as reclaimed LAOs and polyethylene waxes depending on the choice of oligomerization catalyst and polymerization catalyst employed.
- The use of a single feedstock, the same solvents and the same co-catalysts

It will be understood that tandem oligomerization and copolymerization catalysis includes in-situ catalysis. In-situ catalysis means oligomerization and copolymerization catalysis in the same reaction medium. The tandem

oligomerization and copolymerization catalysis may be in-situ concurrent and/ or in-situ consecutive catalysis. Reaction mixture will be understood to include a reaction medium, reaction products and catalyst components. The reaction medium normally includes a solvent.

#### General description of the invention

This invention generally relates to how the need for selectively producing 1-octene or 1-hexene from ethylene and concomitant copolymerization with ethylene can be satisfied by using a separate distinct transition metal oligomerization catalyst system containing a heteroatomic ligand and a separate distinct polymerization catalyst comprising of a transition metal and hetero- or homoatomic ligands.

Thus, according to a first aspect of the invention, there is provided a tandem oligomerization and copolymerization process for the oligomerization of ethylene and in-situ copolymerization of the olefins with ethylene, the process including the step of contacting the olefins with an oligomerization catalyst, which catalyst includes a heteroatomic ligand and a transition metal, and a polymerization catalyst, which catalyst includes a transition metal.

The oligomerization catalyst may be a tetramerization or trimerization catalyst.

The process may include the step of forming the tetramerization or trimerization catalyst

The term "tetramerization" generally refers to the reaction of four ethylene units to yield a linear olefin.

The term "trimerization" generally refers to the reaction of three ethylene units to yield a linear olefin.

The term "copolymerization" generally refers to the reaction of two different monomer units to yield a linear and/or branched polymer.

Referring to the oligomerization catalyst used in this patent embodiment, heteroatomic means a ligand that contains at least two heteroatoms, which can be the same or different, where the heteroatoms may be selected from phosphorus, arsenic, antimony, oxygen, sulphur or nitrogen. More specifically the ligand may be described by the following general formula:  $(R^1)(R^2)A-B-C(R^3)(R^4)$ , where A and C are independently phosphorus, arsenic, antimony, oxygen, sulphur or nitrogen and B is a linking group between A and C. A and/ or C may be a potential donor site.

B may be any linking group, for example hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl linking groups, or inorganic linking groups, including single atom links such as -O-, -S- and -Si-. B may optionally contain any additional potential donor site. Examples of B include methylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine,  $-Si(CH_3)_2-$ ,  $-N(R^5)$  where  $R^5$  is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom (including silicon), a halogen, and the like. B may preferably be  $-N(R^5)$  and  $R^5$  may be a hydrocarbyl or substituted hydrocarbyl.

In addition, B may also be depicted by the following general formula,  $-N(R^6)(Y)$ , where  $R^6$  is a hydrocarbyl group or substituted hydrocarbyl group or a substituted heteroatom (including silicon) and the like.  $R^6$  can consist of ion-pairs or hydrogen acceptor/donor pairs or combinations and extensions of these groups. In this formula, Y may be a cyclopentadienyl, a substituted cyclopentadienyl, an indenyl, a substituted indenyl, a fluorenyl or a substituted fluorenyl group.

Examples of Y include, but are not limited to, butylcyclopentadienyl, methylcyclopentadienyl, 1,3-bistrimethylsilyl cyclopentadiene, 4,7-dimethylcyclopentadienyl, meso-ethylenebis(1-indenyl), rac-dimethylsilylbis(1-indenyl) and diphenylmethyldene(cyclopentadienyl)-(9-fluorenyl).

A and C may be phosphorus.

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl groups. Suitable examples of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> include, but are not limited to, methyl, ethyl, ethylenyl, propyl, butyl, cyclohexyl, benzyl, phenyl, toyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, thiomethyl, thiophenyl, trimethylsilyl, dimethylhydrazyl and the like.

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be independently aromatic or substituted aromatic groups.

Generally, for tetramerization catalysts, the substituents may be preferred to be in the meta or para position. The substituents may be polar or non polar.

Generally, for trimerization catalysts, the substituents may be preferred to be in the ortho position. The substituents may be non polar.

Any of the groups R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may independently be linked to one or more of each other or to the linking group B to form a cyclic structure together with A and C, A and B or B and C.

Examples of ligands, which can be used for tetramerization catalysts are: (phenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(isopropyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(2-ethylhexyl)-P(phenyl)<sub>2</sub> and (phenyl)<sub>2</sub>PN(cyclohexyl)P(phenyl)<sub>2</sub>.

Further examples of ligands, which can be used for tetramerization catalysts are  
(3-methoxyphenyl)<sub>2</sub>PN(methyl)P(3-methoxyphenyl)<sub>2</sub> and (4-methoxyphenyl)<sub>2</sub>PN(methyl)P(4-methoxyphenyl)<sub>2</sub> and (3-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(3-methoxyphenyl)<sub>2</sub> and (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and (4-methoxyphenyl)<sub>2</sub>PN(2-ethylhexyl)P(4-methoxyphenyl)<sub>2</sub> and (4-methylphenyl)<sub>2</sub>PN(methyl)P(3-methoxyphenyl)<sub>2</sub> and (3-methylphenyl)<sub>2</sub>PN(methyl)P(4-methoxyphenyl)<sub>2</sub>.

Examples of ligands, which can be used for trimerisation catalysts are: (o-ethylphenyl)<sub>2</sub>PN(Me)P(o-ethylphenyl)<sub>2</sub>, (o-methylphenyl)<sub>2</sub>PN(Me)P(o-methylphenyl)<sub>2</sub> and (o-isopropylphenyl)<sub>2</sub>PN(Methyl)P(o-isopropylphenyl)<sub>2</sub>.

Examples of suitable polymerization catalysts for the copolymerization of ethylene and the in-situ synthesised  $\alpha$ -olefins include but are not limited to the following:

### ZIEGLER-NATTA CATALYSTS

TiCl<sub>3</sub>-Et<sub>2</sub>AlCl, AlR<sub>3</sub>-TiCl<sub>4</sub>,

### UNBRIDGED METALLOCENES

Bis(cyclopentadienyl)chromium(II),  
Bis(cyclopentadienyl)zirconium Chloride Hydride,  
Bis(cyclopentadienyl)titanium Dichloride,  
Bis(cyclopentadienyl)zirconium Dichloride,  
Bis(cyclopentadienyl)zirconium Dimethyl,  
Bis(*n*-butylcyclopentadienyl)zirconium Dichloride,  
Bis(*n*-dodecylcyclopentadienyl)zirconium Dichloride,  
Bis(ethylcyclopentadienyl)zirconium Dichloride,

Bis(*iso*-butylcyclopentadienyl)zirconium Dichloride,  
Bis(*iso*-propylcyclopentadienyl)zirconium Dichloride,  
Bis(methylcyclopentadienyl)zirconium Dichloride,  
Bis(*n*-octylcyclopentadienyl)zirconium Dichloride,  
Bis(*n*-pentylcyclopentadienyl)zirconium Dichloride,  
Bis(*n*-propylcyclopentadienyl)zirconium Dichloride,  
Bis(trimethylsilylcyclopentadienyl)zirconium Dichloride,  
Bis(1,3-bis(trimethylsilyl)cyclopentadienyl)-zirconium Dichloride,  
Bis(1-ethyl-3-methylcyclopentadienyl)zirconium Dichloride,  
Bis(pentamethylcyclopentadienyl)zirconium Dichloride,  
Bis(pentamethylcyclopentadienyl)zirconium Dimethyl,  
Bis(1-propyl-3-methylcyclopentadienyl)zirconium Dichloride,  
Bis(4,7-dimethylindenyl)zirconium Dichloride,  
Bis(indenyl)zirconium Dichloride,  
Bis(2-methylindenyl)zirconium Dichloride,  
Bis(2-methylindenyl)zirconium Dichloride,  
Cyclopentadienylindenylzirconium Dichloride

#### HALF SANDWICH METALLOCENES

Cyclopentadienylzirconium Trichloride,  
Pentamethylcyclopentadienyl Titanium Trichloride,  
PentamethylcyclopentadienylTitaniumTrimethoxide,  
PentamethylcyclopentadienylTitanium Trimethyl,  
PentamethylcyclopentadienylZirconium Trichloride,  
Tetramethylcyclopentadienylzirconium Trichloride,  
1,2,4-Trimethylcyclopentadienylzirconium Trichloride

### METHYL-BRIDGED METALLOCENES

Diphenylmethylidene(cyclopentadienyl)-(9-fluorenyl)zirconium Dichloride,  
Diphenylmethylidene(cyclopentadienyl)-(indenyl)zirconium Dichloride,  
*iso*-Propylidenebis(cyclopentadienyl)zirconium Dichloride,  
*iso*-Propylidene(cyclopentadienyl)(9-fluorenyl)-zirconium Dichloride,  
*iso*-Propylidene(3-methylcyclopentadienyl)-(9-fluorenyl)zirconium Dichloride

### ETHYL-BRIDGED METALLOCENES

Ethylenebis(9-fluorenyl)zirconium Dichloride,  
*meso*-Ethylenebis(1-indenyl)zirconium Dichloride,  
*rac*-Ethylenebis(1-indenyl)zirconium Dichloride,  
*rac*-Ethylenebis(1-indenyl)zirconium Dimethyl,  
*rac*-Ethylenebis(2-methyl-1-indenyl)zirconium Dichloride,  
*rac*-Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium Dichloride

### SILYL-BRIDGED METALLOCENES

Dimethylsilylbis(cyclopentadienyl)zirconium Dichloride,  
Dimethylsilylbis(9-fluorenyl)zirconium Dichloride,  
*rac*-Dimethylsilylbis(1-indenyl)zirconium Dichloride,  
*meso*-Dimethylsilylbis(2-methylindenyl)zirconium Dichloride,  
*rac*-Dimethylsilylbis(2-methylindenyl)zirconium Dichloride,  
*rac*-Dimethylsilylbis(tetrahydroindenyl)-zirconium Dichloride,  
Dimethylsilylbis(tetramethylcyclopentadienyl)-zirconium Dichloride,  
Diphenylsilyl(cyclopentadienyl)(9-fluorenyl)-zirconium Dichloride,  
Diphenylsilylbis(indenyl)hafnium Dichloride.

The process may include a step of tetramerization of α-olefins and the step of tandem copolymerization of ethylene and the reaction products produced by tetramerization.

The process may include a step of tetramerization of ethylene and the step of tandem copolymerization of ethylene and the reaction products produced by tetramerization.

The process may include a step of trimerization of α-olefins and the step of tandem copolymerization of ethylene and the reaction products produced by trimerisation.

The process may include a trimerization of ethylene and the step of tandem copolymerization of ethylene and the reaction products produced by trimerisation.

The process may include the step of combining a heteroatomic ligand with a transition metal precursor and an activator in the presence of a suitable polymerization catalyst.

In the case of the oligomerization catalyst, the transition metal may be selected from chromium, molybdenum, tungsten, titanium, tantalum and nickel. Preferably, the transition metal is chromium.

In the case of the oligomerization catalyst, the transition metal precursor which, upon mixing with the heteroatomic ligand and an activator, catalyze ethylene oligomerization in accordance with the invention, may be simple inorganic and organic salts, for example halides, acetylacetones, carboxylates, oxides, nitrates, sulfates and the like, as well as co-ordination and organometallic

complexes, for example, chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium hexacarbonyl, molybdenum hexacarbonyl and the like. The preferred transition metal precursor is chromium acetyl acetonate or chromium 2-ethylhexanoate.

The process may include the step of adding a coordination complex of a heteroatomic ligand and a transition metal precursor to a reaction mixture together with a suitable polymerization catalyst, or the step of adding separately to the reactor, a polymerization catalyst, a heteroatomic ligand and a transition metal precursor such that a heteroatomic coordination complex of a transition metal is generated *in-situ*. Typically, the heteroatomic coordination complex for oligomerization is generated *in-situ* and the polymerization catalyst comprises of a pre-formed and purified metal and ligand complex such as is available in the general chemical industry. In the case of the oligomerization catalyst, the transition metal precursor, and heteroatomic ligand are combined (both *in-situ* and *ex-situ*) to typically provide metal/ligand ratios from about 0.01:100 to 10 000:1, and preferably, from about 0.1:1 to 10:1. The polymerization catalyst is combined relative to the tetramerization catalyst in the ratio of 0.1:1 to 1:1000. The hetero atomic ligand may also be formed *in-situ*, for example by the reduction of a phosphineoxide to phosphine.

In the case of the oligomerization catalyst, the heteroatomic ligand can be modified to be attached to a polymer chain (molecular wt. = 1000 or higher) so that the resulting heteroatomic coordination complex of the transition metal is soluble at elevated temperatures, but becomes insoluble at 25°C. This approach would enable the recovery of the complex from the reaction mixture for reuse and has been used for other catalyst as described by D.E. Bergbreiter *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 177-179. In a similar vein these transition metal complexes can also be immobilized by binding the heteroatomic ligands to silica, silica gel, polysiloxane or alumina backbone as demonstrated by C. Yuanyin *et*

al., *Chinese J. React. Pol.*, 1992, 1(2), 152-159 for immobilizing platinum complexes.

The activator for use in the process may in principle be any compound that helps generate an active catalyst when combined with the heteroatomic ligand and the transition metal precursor. Mixtures of activators may also be used. Suitable compounds include organoaluminium compounds, organoboron compounds, organic salts, such as methyl lithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate and the like.

Suitable organoaluminium compounds include compounds of the formula  $\text{AlR}_3$ , where each R is independently  $\text{C}_1\text{-C}_{12}$  alkyl, oxygen or halide, and compounds such as  $\text{LiAlH}_4$  and the like. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-*n*-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, aluminium isopropoxide, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and alumoxanes. Alumoxanes are well known in the art as typically oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic, cages or mixtures thereof. Mixtures of different alumoxanes may also be used in the process.

Examples of suitable organoboron compounds are boroxines,  $\text{NaBH}_4$ , triethylborane, tris(pentafluorophenyl)borane, tributyl borate and the like.

The activator may also be or contain a compound that acts as a reducing or oxidizing agent, such as sodium or zinc metal and the like, or oxygen and the like.

In addition, the activator may also be a binuclear cocatalyst such as a bisborane  $1,4-(C_6F_5)_2BC_6F_4B-(C_6F_5)_2$  as demonstrated by Hongbo Li *et al* in *Journal of the American Chemical Society, ASAP article, 10.1021/ja036289c S0002-7863(03)06289-9, 2003*. This binuclear cocatalyst may be combined with the oligomerization and polymerization catalysts in such a way that a bimolecular specie may be formed that has metal centres in close molecular proximity.

The activator may be selected from aluminoxanes, including alkylaluminoxanes such as methylaluminoxane (MAO), ethylaluminoxane (EAO) Hexylaluminoxane (HAO) and modified alkylaluminoxanes such as modified methylaluminoxane (MMAO).

The aluminoxane may be combined with the oligomerization catalyst metal/polymerization catalyst metal combination in such a way that the ratio may vary relative to the oligomerization catalyst metal only or the polymerization catalyst metal only or in terms of molar fractions of both from 1:1 to 10 000:1 and preferably from about 1:1 to 1000:1.

The process may include the step of adding to the tandem catalyst system a trialkylaluminium compound in amounts of between 0.01 to 2000 mol per mol of aluminoxane. It should however be noted that aluminoxanes generally also contain considerable quantities of the corresponding trialkylaluminium compounds used in their preparation. The presence of these trialkylaluminium compounds in aluminoxanes can be attributed to their incomplete hydrolysis with water. Any quantity of a trialkylaluminium compound quoted in this disclosure is additional to alkylaluminium compounds contained within the aluminoxanes.

The individual components of the tandem catalyst system comprising of the oligomerization catalyst and the polymerization catalyst described herein may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent, in order to give an active catalyst. The mixing of the

catalyst components can be conducted at any temperature between -78°C and 150°C.

The tandem catalyst system, comprising of the oligomerization catalyst and polymerization catalyst, in accordance with the invention, may be immobilized by supporting it on a support material, for example, silica, alumina, MgCl<sub>2</sub>, zirconia or mixtures thereof, or on a polymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene) or on a natural or artificial clay such as LAPONITE™. The tandem catalyst system can be formed in-situ in the presence of the support material, or the support can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. In some cases, the support material can also act as a component of the activator. This approach would also facilitate the recovery of the catalyst from the reaction mixture for reuse. The concept was successfully demonstrated with a chromium-based ethylene trimerization catalyst by T. Monoi and Y. Sasaki, *J. Mol. Cat.A:Chem.*, 1987, 109, 177-179. In some cases, the support can also act as a catalyst component, for example where such supports contain aluminoxane functionalities or where the support is capable of performing similar chemical functions as an aluminoxane, which is for instance the case with IOLA™ (a commercial product from GRACE Davison Catalysts).

The reaction products, or in other words olefin oligomers and polymer, as described herein, may be prepared with the disclosed catalyst system by homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may therefore also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, hexane, heptane, cyclohexane, octane, octene and the like.

The process may be carried out at pressures from atmospheric to 150 barg. Ethylene pressures in the range of 10-70 bar are preferred. Particularly preferred pressures range from 30-50 barg.

The process may be carried out at temperatures from -78 °C to 250 °C. Temperatures in the range of 20-130 °C are preferred. Particularly preferred temperatures range from 35-100°C.

In a preferred embodiment of the invention, the heteroatomic coordination complex that constitutes the oligomerization catalyst component of the tandem catalyst system, and reaction pressures is selected such that the yield of 1-octene or 1-hexene, as the case may be, from ethylene is greater than 25 mass %, preferably greater than 50 mass %. In this regard yield refers to grams of 1-octene or 1-hexene formed per 100g of total reaction product formed. This yield is typically needed to produce LLDPE.

Although the tandem catalyst system, its individual components, reagents, solvents and reaction products are generally employed on a once-through basis, any of these materials can, and are indeed preferred to, be recycled to some extent in order to minimize production costs.

The process may be carried out in a plant which includes any type of reactor. Examples of such reactors include, but are not limited to, batch reactors, semi-batch reactors and continuous reactors. The plant may include, in combination a)

a reactor, b) at least one inlet line into this reactor for olefin reactant and the catalyst system, c) effluent lines from this reactor for oligomerization reaction products, and d) one or more separators to separate the oligomerization reaction products and the polymerization reaction products, wherein the catalyst system may include a heteroatomic coordination complex of a transition metal salt constituting the oligomerization catalyst component and a separate and distinct transition metal and ligand complex constituting the polymerization catalyst component and an activator, as described herein.

In another embodiment of the process the reactor and a separator may be combined to facilitate the simultaneous formation of reaction products and separation of these compounds from the reactor. This process principle is commonly known as reactive distillation when the reaction is a homogeneous liquid phase reaction. When the catalyst system exhibits no solubility in the solvent or reaction products, and is fixed in the reactor so that it does not exit the reactor with the reactor product, solvent and unreacted olefin, the process principle is commonly known as catalytic distillation.

In another embodiment of this invention, the oligomerization reaction may be carried out in a reactor. The reaction mixture of this oligomerization reactor may then serve (without any further process steps such as purification) as the feed for separate polymerization reactors such as multiple sequential reactors, cascade reactors, jetloop reactors and tubular reactors to which the polymerization catalyst is independently added. In this instance the tandem catalysis is thus conducted in two sequential reactors. The use of two separate reactors for a tandem oligomerisation copolymerisation process may facilitate a better control of the properties of the final copolymer product.

According to a further aspect of the invention, there is provided a tandem oligomerization and copolymerization catalyst system, as described above, for the oligomerization of olefins and the tandem copolymerization of the products of

the oligomerization process and ethylene. The catalyst system may include as one component, a heteroatomic ligand as described above and a transition metal constituting the oligomerization catalyst system and another component, a transition metal and homo- or heteroatomic ligand constituting the polymerization system. The catalyst system may also include an activator as described above.

#### **Detailed description of the invention**

The invention is now described by way of example.

In the examples that follow all procedures were carried out under inert conditions, using pre-dried reagents.

#### **Example 1**

In this example, an amount of 0.011 mmol Chromium acetylacetone Cr(acac)<sub>3</sub> or 3.8 mg was combined with 0.022 mmol (phenyl)<sub>2</sub>PN(iso-propyl)P(phenyl)<sub>2</sub> or 9.39 mg in a Schlenk tube under an Argon atmosphere with 10 ml anhydrous toluene as solvent. The metal salt and the ligand was stirred for 5 minutes and then added to a Parr autoclave (300 ml capacity) containing at least two inlets, under inert conditions. The autoclave was filled *a priori* with 70 ml anhydrous toluene as solvent. Separately, 2 ml of a 0.26 mmol/100 ml solution of dimethylsilylbis(2-methyl(4,5)benzoindenyl) zirconium dichloride (0.026 mmol) was added to 18 ml anhydrous toluene in a separate reservoir connected to the inlet of an HPLC pump. Approximately 1200 eq methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was heated to 45 °C, sealed and pressurized to a pressure of 510 PSI with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerization catalyst solution was added to the autoclave through a separate inlet connected to the outlet of the HPLC pump.

The polymerization catalyst was added at a rate of 0.66 ml/min over a period of 30 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis.

Following analysis of the liquid component by gas chromatography, it was found that 0.72 g 1-hexene was left as well as 2.73 g 1-octene. The amount of polymer collected was found to be 23.16 g with a melting point of 126 °C and an amount of 1-octene incorporated determined by C13 nuclear magnetic resonance spectroscopy of 3.83 %.

### Example 2

In this example, a solution of 0.044 mmol of (phenyl)<sub>2</sub>PN(iso-propyl)P(phenyl)<sub>2</sub> in 20 ml anhydrous toluene and a solution of 0.022 mmol of Cr(acac)<sub>3</sub> in 20 ml anhydrous toluene together with 30 ml anhydrous toluene was added to a Parr autoclave (300 ml capacity). At the same time, 10 ml (0.026 mmol) of tetramethylcyclopentadienyldimethylsilyltetrabutylamido titanium dichloride was added to an external reservoir along with 10 ml anhydrous toluene. The external reservoir was connected to the inlet of an HPLC pump. Approximately 1200 eq methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was heated to 45 °C, sealed and pressurized to a pressure of 620 PSI with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerization catalyst solution was added to the autoclave through a separate inlet connected to the outlet of the HPLC pump.

The polymerization catalyst was added at a rate of 0.66 ml/min over a period of 30 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis.

The liquid component collected was analyzed by gas chromatography and found to contain 6 g residual 1-octene and 2 g residual 1-hexene. Analysis of the

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polymer revealed a melting point of 99 °C and 2.39 % incorporation of  $\alpha$ -olefin. The amount of polymer collected was 24.53 g.

**Example 3**

To provide a suitable support material for the metallocene catalysts employed in this invention, an artificial clay (LAPONITE<sup>TM</sup>) was dried overnight at 300 °C after which it was cooled to room temperature. An amount of 10 g of the dry LAPONITE powder was brought into contact with 50 ml of a solution of dimethylsilylbis(2-methyl(4,5)benzoindenyl) zirconium dichloride (0.1 mmol/ 100 ml). The bright yellow solution was stirred with a magnetic stirring bar in a Schlenk tube under inert conditions. It was observed that the solution quickly lost most of its colour and that the white LAPONITE<sup>TM</sup> powder took on the yellow colour of the solution.

The excess pale yellow liquid was decanted off and the powder was washed 4 times with portions of anhydrous toluene until no colour change was observed. After this, the yellow powder was transferred to Parr autoclave (300 ml capacity) containing 95 ml anhydrous toluene. To the dispersion was added 5 ml MAO after which the autoclave was sealed, heated to 100 °C and pressurized with ethylene to a pressure of 620 PSI and then closed. An immediate exotherm was observed that reached a maximum of 175 °C after a few minutes. The pressure dropped from 620 PSI to 40 PSI within 10 minutes. A large amount of polymer (34 g) with a high melting point (136 °C) was obtained.

DATED THIS 6<sup>TH</sup> DAY OF OCTOBER, 2003

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# **Document made available under the Patent Cooperation Treaty (PCT)**

International application number: PCT/ZA03/000188

International filing date: 19 December 2003 (19.12.2003)

Document type: Certified copy of priority document

Document details: Country/Office: ZA  
Number: 2003/7773  
Filing date: 06 October 2003 (06.10.2003)

Date of receipt at the International Bureau: 05 July 2004 (05.07.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



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Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse